

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

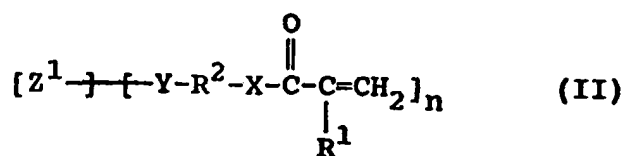
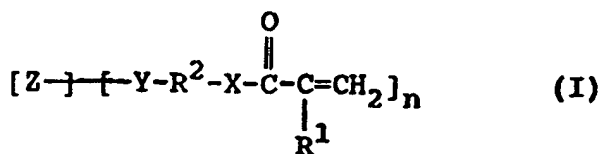
(51) International Patent Classification ⁶ : C07D 303/00	A2	(11) International Publication Number: WO 98/28286 (43) International Publication Date: 2 July 1998 (02.07.98)
<p>(21) International Application Number: PCT/EP97/07286</p> <p>(22) International Filing Date: 22 December 1997 (22.12.97)</p> <p>(30) Priority Data: 08/773,524 23 December 1996 (23.12.96) US</p> <p>(71) Applicant (for all designated States except PL US): SAR-TOMER COMPANY, INC. [US/US]; Oaklands Corporate Center, 502 Thomas Jones Way, Exton, PA 19341 (US).</p> <p>(71) Applicant (for PL only): CRAY VALLEY S.A. [FR/FR]; Tour Total, 24, cours Michelet, F-92800 Puteaux (FR).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): CESKA, Gary, W. [US/US]; 310 Long Ridge, Exton, PA 19341 (US). FAN, Mingxin [CN/US]; 49 Sheffield Lane, West Chester, PA 19380 (US). HORGAN, James [US/US]; 805 Copeland School Road, West Chester, PA 19380 (US).</p> <p>(74) Agent: CHAILLOT, Geneviève; Cabinet Chaillot, 16-20, avenue de l'Agent Sarre, Boîte postale 74, F-92703 Colombes Cedex (FR).</p>		<p>(81) Designated States: CA, CN, JP, KR, MX, PL, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published Without international search report and to be republished upon receipt of that report.</p>

(54) Title: UNSATURATED (METH)ACRYLATE ESTERS CONTAINING EPOXIDIZED CYCLIC GROUPS AND PROCESS FOR PREPARING

(57) Abstract

A process of making compounds of formula (I), wherein Z is an unsubstituted or substituted n-valent cyclic moiety bearing at least one endocyclic oxirane group; Y is O, S, NH, (Ia) or (Ib); R² is a divalent linking group; X is O, S or NH; R¹ is H or (C₁-C₆) alkyl; and n is an integer from 1 to 6, Z being mono- to hexavalent respectively, it being possible for -Y-R² to represent a single bond, comprises reacting a compound of formula (II), wherein Z¹ is a cyclic moiety bearing at least one endocyclic C=C group; and Y, R², X, R¹ and n are as defined above with hydro-

gen peroxide in the presence of (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide; (b) phosphoric acid or a salt thereof; and (c) at least one phase transfer catalyst.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

UNSATURATED (METH)ACRYLATE ESTERS CONTAINING EPOXIDIZED CYCLIC GROUPS AND PROCESS FOR PREPARING.

This invention relates to epoxidation of unsaturated (meth)acrylate esters.

5 (Meth)acrylate monomers which have epoxide functional groups are widely used in industry as chemical intermediates for synthetic materials. Traditionally, these monomers are being produced from epichlorohydrin via coupling with corresponding salts. Epoxidation of unsaturated organic
10 substrates without (meth)acrylate functional groups is much easier due to the lack of (meth)acrylate functional group polymerization initiated by peroxide or radicals generated in situ. US 2,833,787 and 2,833,788 describe the epoxidation of nonconjugated ethylenic compounds by hydrogen peroxide and
15 water soluble sodium pertungstate at a pH of between 3 and 7. Similarly, unsaturated acids were epoxidized by hydrogen peroxide and sodium tungstate (J. Org. Chem., vol. 24, 54).

Olefin epoxidation using hydrogen peroxide and a water soluble alkali metal tungstate in the presence of a
20 phase transfer agent was reported (J. Org. Chem., vol. 48, 3831 and J. Org. Chem., vol. 50, 2688). Similarly, water-soluble molybdophosphoric and tungstophosphoric acid (hetero polyacids) were used in the catalytic epoxidation of olefins using hydrogen peroxide (J. Org. Chem., vol. 52, 1868 and
25 vol. 53, 3587).

The epoxidation of unsaturated (meth)acrylate esters using peracetic acid was described in US 3,459,775 in very low yield. US 5,283,360 describes the selective epoxidation of unsaturated (meth)acrylates using hydrogen
30 peroxide in the presence of water soluble alkali metal molybdates and tungstates as well as heteropolyacid for cyclic substrates and phase transfer agent. According to US 5,283,360, conversion was less than 100% and residual allylic compound was present.

35 US Patents 5,783,360 and 5,510,516 to Caubere et al, show epoxidation of unsaturated (meth)acrylate esters with hydrogen peroxide using a catalyst system which comprises

alkali metal salts of tungstic or molybdic acids and a heteropolyacid. Caubere et al do not show (meth)acrylates which have been alkoxyated, nor do they show phosphoric acid.

GB application 2 055 821 A by Venturello et al,
5 shows epoxidation of olefins with hydrogen peroxide using a catalyst system consisting of W, Mo, or V, and at least one derivative of P or As. This application does not show epoxidation of (meth)acrylates or alkoxyated compounds.

One of the problems of the prior art processes is
10 low catalyst lifetime and low catalytic conversion. Low conversion results in contamination with the starting material which causes crosslinking during free radical polymerization. Prior art catalytic systems include water soluble alkali metal salts of molybdates and tungstates as well as their
15 heteropolyacids. In the presence of phase transfer agent, the conversion is low and residual unsaturated (meth)acrylate remains in the initial product mixture, resulting in low stability and crosslinking in some applications. Prior art in this field requires water soluble alkali metal salts of
20 molybdates and tungstates and their heteropolyacids.

It is therefore an object of the present invention to provide an improved method of selectively epoxidizing compounds having acrylate or methacrylate groups.

It is also an object of the invention to provide
25 a new class of (meth)acrylates containing epoxide functionalities.

A further object of the invention is to provide a method of epoxidizing (meth)acrylates which have improved catalyst life and higher than previously achieved yields.

30 These objects, and others which will become apparant from the following disclosure are achieved by the present invention which comprises in one aspect a process for selectivity epoxidizing (meth)acrylate monomers using hydrogen peroxide as oxidizing agent and a catalyst system comprising
35 water insoluble tungstic acid or molybdic acid or molybdenum oxide in combination with phosphoric acid or a salt thereof in the presence of phase transfer agent.

Another aspect of the invention is a process for epoxidizing (meth)acrylate monomers which results in complete conversion comprising using insoluble tungstic acid or tungsten oxide (or molybdic acid or molybdenum oxide) and phosphoric acid or a metal salt thereof with or without any acidity adjustment.

The current invention will result in complete conversion of unsaturated (meth)acrylate esters to (meth)acrylate epoxides using insoluble tungstic acid or molybdic acid or molybdenum oxide and phosphoric acid or a metal salt thereof with or without any acidity adjustment.

The catalyst composition used in the process of the invention is highly effective and selective, which is very advantageous in the epoxidation of unsaturated (meth)acrylate monomers.

The new method involves low level of catalyst composition. Furthermore, no organic acid and/or peracid is used which results in simple product workup and process.

The present invention uses hydrogen peroxide in the presence of

- (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide ;
- (b) phosphoric acid or a metal salt thereof ; and
- (c) at least one phase transfer catalyst.

The epoxidation of unsaturated (meth)acrylates with hydrogen peroxide in the presence of tungsten catalyst or molybdenum catalyst, phosphoric acid or its salt, and phase transfer catalyst can be performed at any temperature which is sufficient to react, however, particularly suitable temperatures are between 0°C and 100°C, preferably from 25°C to 70°C and more particularly from 50 to 70°C. The reaction takes place faster at higher temperature and requires shorter time to complete, the reaction is typically exothermic and slow addition of hydrogen peroxide is preferred to control the exotherm. At higher temperature, hydrogen peroxide undergoes decomposition. The reaction can be performed at pressures from subatmospheric to superatmospheric pressures ; however, the reaction is preferably carried out at atmospheric pressure.

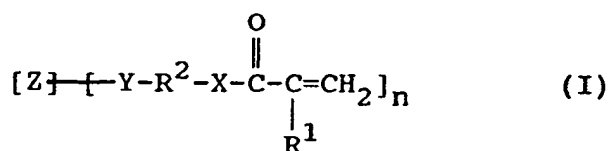
The epoxidation can be performed with or without solvent, solvent can be used to reduce the viscosity, if solvent is needed, a water-immiscible organic solvent such as chlorinated hydrocarbons, ethers, glycol ethers, aliphatic and aromatic hydrocarbons, alkyl esters, and combinations thereof. Particular suitable organic solvents are toluene, chlorobenzene, chloroform, methylene chloride, heptane, and the like.

Hydrogen peroxide solution is used as oxidant in the concentration in water of 5 to 70% by weight. The amount of hydrogen peroxide can vary depending on the desired degree of epoxidation, typically from 0.1 to 1.5, and particularly from 1 to 1.5, equivalent per C=C in Z^1 in the starting material.

The phase transfer catalyst can be used from 0.001 to 1.5, preferably 0.05 to 1.0, equivalent per equivalent of carbon carbon double bond in Z^1 . Suitable phase transfer catalysts includes quaternary ammonium salts, quaternary phosphonium salts, polyethers and ether derivatives such as polycondensates of polyethers or functional polyethers, and the like. Examples of phase transfer catalysts include, for example, trioctylmethylammonium chloride, trioctylmethylammonium bromide, trioctylmethylammonium iodide, trioctylmethylammonium hydrogen sulfate, trioctylmethylammonium nitrate, tetrahexylammonium chloride, tetrahexylammonium bromide, tetrahexylammonium iodide, tetrahexylammonium hydrogen sulfate, tetrahexylammonium nitrate, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium nitrate, tetrabutylammonium hydrogen sulfate, dioctadecyldimethylammonium chloride, dioctadecyldimethylammonium bromide, dioctadecyldimethylammonium nitrate, dioctadecyldimethylammonium hydrogen sulfate, dihexadecyldimethylammonium chloride, dihexadecyldimethylammonium bromide, dihexadecyldimethylammonium nitrate, dihexadecyldimethylammonium hydrogen sulfate, trioctylmethylphosphonium chloride, trioctylmethylphosphonium bromide, trioctylmethylphosphonium nitrate, trioctylmethylphosphonium hydrogen sulfate, tetrahexyl-

phosphonium chloride, tetrahexylphosphonium bromide, tetrahexylphosphonium nitrate, tetrahexylphosphonium hydrogen sulfate, tetrabutylphosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium nitrate, tetrabutylphosphonium hydrogen sulfate, tetrabutylphosphonium iodide, dioctadecyldimethylphosphonium chloride, dioctadecyldimethylphosphonium bromide, dioctadecyldimethylphosphonium nitrate, dioctadecyldimethylphosphonium hydrogen sulfate, dihexadecyldimethylphosphonium chloride, dihexadecyldimethylphosphonium bromide, dihexadecyldimethylphosphonium nitrate, dihexadecyldimethylphosphonium hydrogen sulfate, tetraalkylammonium hydroxide, tetraalkylammonium tribromide, tetraalkylammonium trifluoromethanesulfonate, and any combination thereof.

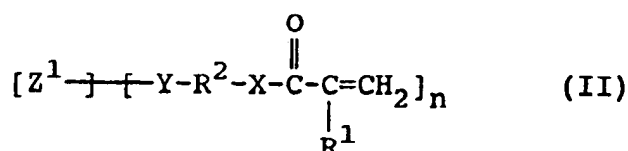
The method of the invention comprises a process of making compounds of the formula :



wherein :

- Z is an unsubstituted or substituted n-valent cyclic moiety bearing at least one endocyclic oxirane group;
- Y is O, S, NH, $-\overset{\overset{O}{\parallel}}{O}-C-$ or $-C-\overset{\overset{O}{\parallel}}{O}-$;
- R^2 is a divalent linking group ;
- X is O, S or NH ;
- R^1 is H or (C_1-C_6) alkyl ; and
- n is an integer from 1 to 6, Z being mono- to hexavalent respectively,

it being possible for $-Y-R^2-$ to represent a single bond, characterized by the fact that it comprises reacting a compound of the formula :



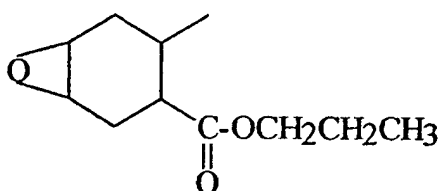
wherein :

- Z^1 is an unsubstituted or substituted n-valent cyclic moiety bearing at least one endocyclic C=C group ; and
- Y, R^2 , X, R^1 and n are as defined above,

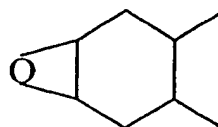
5 with hydrogen peroxide in the presence of :

- (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide ;
- (b) phosphoric acid or a salt thereof ; and
- (c) at least one phase transfer catalyst.

10 Z may be an epoxidized dicyclopentenyl group or an epoxidized unsubstituted or substituted cyclohexenyl group. According to an embodiment of the present invention, the process leads to compound (I) wherein Z is



or to a compound (I) wherein Z is



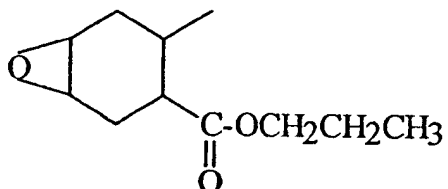
15 or to a mixture of both.

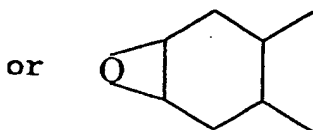
The resultant compounds (I) are novel, except when Z is an epoxidized dicyclopentenyl group, Y is O, R^2 is C_1-C_{10} alkylene, X is O, and R^1 is H or methyl.

Preferred compounds are those wherein R^1 is H or
 20 methyl, i.e., acrylates or methacrylates, and those wherein X is O and R^2 is an alkylene, or (poly)oxyalkylene having from 1 to 20 carbon atoms and more particularly alkylenes having from 2 to 12 carbon atoms or (poly)oxyalkylenes having from 4 to 20 carbon atoms.

25 Especially preferred compounds (I) are those wherein Z is unsubstituted or substituted epoxidized cyclohexenyl groups. While any substituent can be used, preferred

30 one alkyl or ester, for example, methyl or $-C(=O)-O-CH_2CH_2CH_3$

ester. Compounds wherein Z =  can be cited.



can be cited.

Phosphoric acid or its various salts can be used from 0.001 to 0.5 equivalent per equivalent of carbon carbon double bond. Sodium or potassium salts of monobasic, dibasic or tribasic salts of phosphoric acid can also be used. The final pH can be adjusted by other acids or bases to a value between 0 and 5.

Tungstic acid or its metal salts can be used as the metal catalysts, the metal salts are water soluble and the acid is not. Molybdic acid or molybdenum oxide can also be used as metal catalyst. The typical catalyst is used from 0.005 to 1% and the preferred catalyst is tungstic acid which is not water-soluble or molybdic acid.

The epoxidized unsaturated (meth)acrylates can be used in a variety of applications, such as coatings, epoxy/amine cure, cationic cure, and chemical intermediates for polymers and oligomers.

One aspect of the invention is composition comprising compounds of formula (I) for use in the above-mentioned applications.

The compounds of formula (I) can be used to make novel polymers, both homo- and copolymers. Especially useful polymers are copolymers of a compound of formula I and one or more acrylates, methacrylates, epoxy compounds. Also preferred are copolymers of : (A) a compound of formula (I) ; (B) an epoxy compound not containing an acrylate or methacrylate group, and (C) an acrylate or methacrylate compound not containing an epoxy group.

The polymers can be prepared by exposing the monomer or monomer mixture to radiation according to methods known in the art.

In some embodiments, the monomers are first reacted
5 via free radical polymerization and then cured via the epoxy groups. In other embodiments the epoxy groups can be polymerized using cationic initiator.

A preferred embodiment is when both free radical initiator and cationic initiator are present and the mixture
10 is exposed to radiation to form a cured polymer.

The cured polymers can be used for coatings, sealants, adhesives, inks, and the like.

The following non-limiting examples are presented to illustrate a few embodiments of the invention. All parts
15 and percentages are by weight unless otherwise indicated.

EXAMPLE 1

Epoxidation of 2-(dicyclopentenylloxy)ethyl methacrylate

In a four-necked flask tungstic acid (1.50 g), sodium hydroxide (25%, 0.75 ml), and phosphoric acid (85%,
20 0.50 ml) were added, followed by addition of 2-(dicyclopentenylloxy) ethyl methacrylate (131.0 g, 0.5 mole), toluene (131.0 g), and trioctylmethyl ammonium chloride (1.50 g). The resultant mixture was stirred to form a yellow mixture and heated to 60°C, after which hydrogen peroxide (30%, 100.0 ml)
25 was added slowly over 50 min. The reaction mixture was stirred at 60°C for 2 ½ hours.

GC analysis showed no starting material left and 100% conversion to epoxide was obtained.

EXAMPLE 2Epoxidation of dicyclopentenyl methacrylate

Following the same procedure, dicyclopentenyl methacrylate was epoxidized with 100% conversion.

5

EXAMPLE 3Epoxidation of dicyclopentenyl acrylate

Following the same procedure, dicyclopentenyl acrylate was epoxidized with 100% conversion.

EXAMPLE 410 Epoxidation of 2-(dicyclopentenylloxy) ethyl methacrylate

Example 1 was repeated without sodium hydroxide. The material was epoxidized with 100% conversion.

EXAMPLE 5Synthesis of unsaturated methacrylate ester

15 In a four-necked flask, tetrahydrophthalic anhydride (152.1 g), hydroxyethyl methacrylate (130.0 g), and methoxyphenol (0.30 g) were added and stirred, and air sparge was applied while stirring. The mixture was heated to 100°C for six hours. IR showed no anhydride starting material left.

20 To the above product, 1-propanol (84.0 g), methoxyphenol (2.0 g), toluene (75.0 g), heptane (75.0 g), methanesulfonic acid (70%, 10.0 g) were added, air sparge applied, the mixture was stirred and refluxed. Water was removed azeotropically during the reaction and the
25 esterification reaction completed in 5.0 hours. The final mixture was neutralized and washed with 25% NaOH and solvent

was stripped at 3.33×10^3 Pa (25 mmHg) at 95°C. 273.0 g clear light yellow unsaturated methacrylate was obtained.

EXAMPLE 6

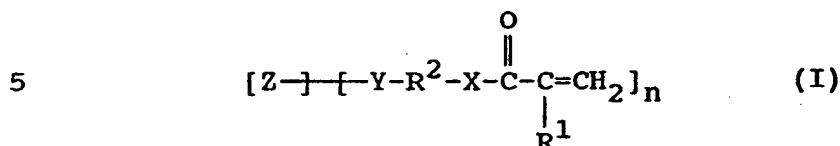
Epoxidation of unsaturated methacrylate ester from Example 5

5 100.0 g unsaturated methacrylate ester from Example 5, 100.0 g toluene, 0.80 g trioctylmethyl ammonium chloride, 0.80 g tungstic acid, 0.40 g sodium hydroxide (25%), and 0.40 g phosphoric acid (85%) were added to a reactor, and the mixture was stirred and heated to 60°C. Then 100 ml H₂O₂
10 (30%) was slowly added within 30 min. and the temperature was controlled at 60°C. The reaction mixture was kept at 60°C for additional 3 ½ hours. The unsaturated methacrylate was completely epoxidized based on GC analysis.

15 While the invention has been described in sufficient detail for those skilled in the art to make and use it, various modifications, alternatives, and improvements should become readily apparent without departing from the spirit and scope of the invention as set forth in the following claims.

CLAIMS

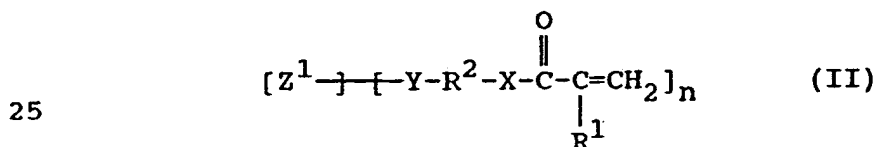
1 - Process of making compounds of the formula :



wherein :

- Z is a unsubstituted or substituted n-valent cyclic moiety bearing at least one endocyclic oxirane group ;
- Y is O, S, NH, $-\overset{\overset{O}{\parallel}}{O}-C-$ or $-C-\overset{\overset{O}{\parallel}}{O}-$;
- R² is a divalent linking group ;
- X is O, S or NH ;
- R¹ is H or (C₁-C₆) alkyl ; and
- n is an integer from 1 to 6, Z being mono- to hexavalent respectively,

it being possible for -Y-R²- to represent a single bond,
 20 characterized by the fact that it comprises reacting a compound of the formula :

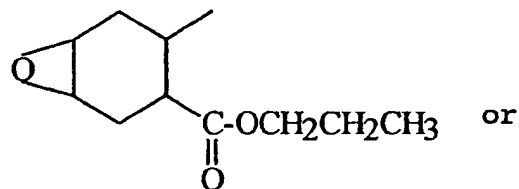


wherein :

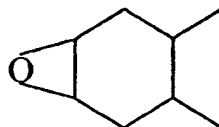
- Z¹ is a cyclic moiety bearing at least one endocyclic C=C group ; and
 - Y, R², X, R¹ and n are as defined above,
- with hydrogen peroxide in the presence of :
- (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide ;
 - (b) phosphoric acid or a salt thereof ; and
 - (c) at least one phase transfer catalyst.

2 - Process according to claim 1, characterized by the fact that Z is an epoxidized dicyclopentenyl group or an epoxidized unsubstituted or substituted cyclohexenyl group.

3 - Process according to claim 2, characterized by the fact that leads to compound (I) wherein Z is



to a compound (I) wherein Z is



5 or to a mixture of both.

4 - Process according to anyone of claims 1 to 3, characterized by the fact that R^2 is an alkylene or (poly)alkylene group having from 1 to 20 carbon atoms, and particularly alkylene group having from 1 to 12 carbon atoms and (poly)oxyalkylene groups having from 4 to 20 carbon atoms.

5 - Process according to anyone of claims 1 to 4, characterized by the fact that said hydrogen peroxide is introduced in an amount of about 1 to 1.5, particularly of about 1 to 1.5, equivalent per equivalent of C=C group in Z^1 .

6 - Process according to anyone of claims 1 to 5, characterized by the fact that the reaction is conducted at a temperature of about 0°C to 100°C.

7 - Process according to claim 6, characterized by the fact that the reaction is conducted at a temperature of about 25°C to 70°C, particularly at a temperature of about 50 to 70°C.

8 - Process according to anyone of claims 1 to 7, characterized by the fact that the phase transfer catalyst is present in an amount of about 0.001 to 1.5, particularly of about 0.05 to 1.0, equivalent per equivalent of C=C group in Z^1 .

9 - Process according to anyone of claims 1 to 8, characterized by the fact that the phase transfer catalyst is selected from the group consisting of quaternary ammonium salts, quaternary phosphonium salts, polyethers and polyether derivatives.

10 - Process according to anyone of claims 1 to 9, characterized by the fact that the reaction is conducted in the presence of a water immiscible organic solvent.

11 - Process according to claim 10, characterized
5 by the fact that the water immiscible organic solvent is selected from the group consisting of chlorinated hydrocarbons, ethers, glycol ethers, aliphatic and aromatic hydrocarbons, alkyl esters and combinations thereof, particularly from the group consisting of toluene,
10 chlorobenzene, chloroform, heptane and methylene chloride.

12 - Process according to anyone of claims 1 to 11, characterized by the fact that the phosphoric acid or phosphoric acid salt comprises about 0.001 to 0.5 equivalent per equivalent of C=C group in Z¹.

13 - Process according to anyone of claims 1 to 12, characterized by the fact that the phosphoric acid salt is a sodium or potassium monobasic, dibasic, or tribasic phosphoric acid salt.

14 - Process according to anyone of claims 1 to 13,
20 characterized by the fact that the pH of the reaction is adjusted by acids or bases to a value between 0 and 5.

15 - Process according anyone of claims 1 to 14, characterized by the fact that the tungstic acid or tungsten oxide or molybdic acid or molybdenum oxide is present in an
25 amount of about 0.005 to 1% based on weight of compound of formula (II).

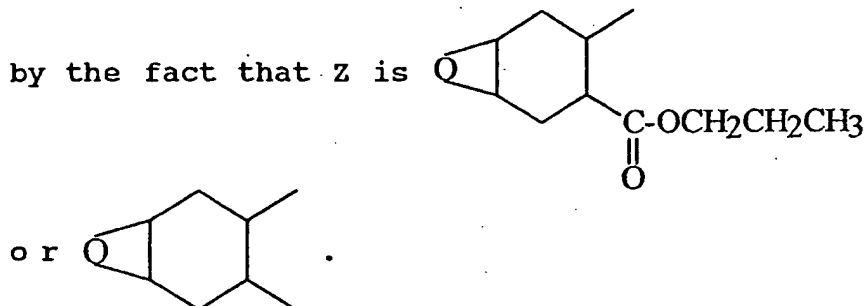
16 - Compound of formula (I) as defined in anyone of claims 1 to 4, except for compounds wherein Z is an epoxidized dicyclopentenyl group, Y is O, R² is C₁-C₁₀
30 alkylene, X is O, and R¹ is H or methyl.

17 - Compound of claim 16, characterized by the fact that R¹ is H or methyl.

18 - Compound of claims 16 or 17, characterized by the fact that X is O and R² is an alkylene or
35 (poly)oxyalkylene having a number of carbons from 1 to 20, such as an alkylene having from 1 to 10 carbon atoms or a (poly)oxyalkylene having from 4 to 20 carbon atoms.

19 - Compound of anyone of claims 16 to 18, characterized by the fact that Z is epoxidized cyclohexenyl group or epoxidized substituted cyclohexenyl group, such as epoxidized ester substituted or alkyl-substituted cyclohexenyl group.

20 - Compounds according to claim 19, characterized



21 - Composition comprising at least one compound as defined in anyone of claims 16 to 19 or obtained by a process as defined in anyone of claims 1 to 15.

22 - Composition comprising a polymer of a compound as defined in anyone of claims 16 to 19 or obtained by a process as defined in anyone of claims 1 to 15.

23 - Composition of claim 22, characterized by the fact that the polymer is a copolymer of a compound of formula (I) and one or more acrylates, methacrylates, epoxy compounds.

24 - Composition of anyone of claims 22 and 23, characterized by the fact that the polymer is prepared by exposing the compound and any comonomers to radiation.

25 - Composition of anyone of claims 22 to 24, characterized by the fact that the polymer is a copolymer of :

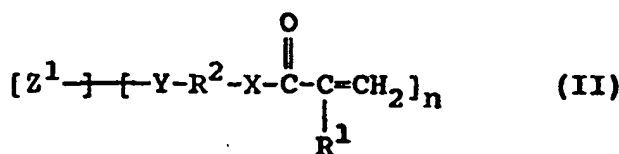
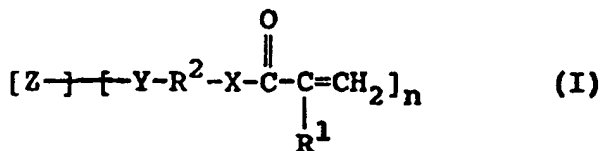
- (A) a compound of formula (I) ;
- (B) an epoxy compound not containing an acrylate or methacrylate group ; and
- (C) an acrylate or methacrylate compound not containing an epoxy group.

26 - Composition of claim 25, characterized by the fact that the polymer is prepared by exposing a mixture of (A), (B) and (C) to radiation in the presence of free radical initiator and cationic initiator.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07D 301/12, 303/16, 303/20, 303/48, C08F 120/18, 220/18	A3	(11) International Publication Number: WO 98/28286 (43) International Publication Date: 2 July 1998 (02.07.98)
(21) International Application Number: PCT/EP97/07286 (22) International Filing Date: 22 December 1997 (22.12.97) (30) Priority Data: 08/773,524 23 December 1996 (23.12.96) US (71) Applicant (for all designated States except PL US): SAR- TOMER COMPANY, INC. [US/US]; Oaklands Corporate Center, 502 Thomas Jones Way, Exton, PA 19341 (US). (71) Applicant (for PL only): CRAY VALLEY S.A. [FR/FR]; Tour Total, 24, cours Michelet, F-92800 Puteaux (FR). (72) Inventors; and (75) Inventors/Applicants (for US only): CESKA, Gary, W. [US/US]; 310 Long Ridge, Exton, PA 19341 (US). FAN, Mingxin [CN/US]; 49 Sheffield Lane, West Chester, PA 19380 (US). HORGAN, James [US/US]; 805 Copeland School Road, West Chester, PA 19380 (US). (74) Agent: CHAILLOT, Geneviève; Cabinet Chaillot, 16-20, av- enue de l'Agent Sarre, Boîte postale 74, F-92703 Colombes Cedex (FR).		(81) Designated States: CA, CN, JP, KR, MX, PL, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims</i> <i>and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 13 August 1998 (13.08.98)
(54) Title: UNSATURATED (METH)ACRYLATE ESTERS CONTAINING AT LEAST ONE EPOXIDIZED CYCLIC GROUP AND PROCESS FOR PREPARING THEM (57) Abstract A process of making compounds of formula (I), wherein Z is an unsub- stituted or substituted n-valent cyclic moiety bearing at least one endocyclic oxirane group; Y is O, S, NH, (Ia) or (Ib); R ² is a divalent linking group; X is O, S or NH; R ¹ is H or (C ₁ -C ₆) alkyl; and n is an integer from 1 to 6, Z be- ing mono- to hexavalent respectively, it being possible for -Y-R ² to represent a single bond, comprises reacting a com- pound of formula (II), wherein Z ¹ is a cyclic moiety bearing at least one en- docyclic C=C group; and Y, R ² , X, R ¹ and n are as defined above with hydro- gen peroxide in the presence of (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide; (b) phosphoric acid or a salt thereof; and (c) at least one phase transfer catalyst.		



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 97/07286

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D301/12 C07D303/16 C07D303/20 C07D303/48 C08F120/18
C08F220/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D C08F C07F C08G C08L C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 14 18 698 A (CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GMBH) 10 October 1968 see examples 1-3 & DATABASE CHEM. ABS. REGISTRY American Chemical Society see RN: 1443-40-9, 1147-02-0, 2389-91-5 ---	16
X	US 3 230 202 A (S.W. TINSLEY ET AL.) 18 January 1966 see compound of claim 7 & DATABASE CHEM. ABS. REGISTRY American Chemical Society see RN: 7534-87-4 --- -/-	16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

28 May 1998

Date of mailing of the international search report

25.06.98

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Frelon, D

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/07286

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 479 166 A (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY, INC.) 8 April 1992 see page 18; example 5 & DATABASE CHEM. ABS. REGISTRY American Chemical Society see RN: 141952-18-3 ---	16
X	DATABASE WPI Week 9023 Derwent Publications Ltd., London, GB; AN 90-174259 XP002066023 & JP 02 113 019 A (TOSOH CORP.) , 25 April 1990 & DATABASE CHEM. ABS. REGISTRY American Chemical Society see RN: 129219-53-0 ---	16
X	DATABASE CHEM. ABS. REGISTRY American Chemical Society XP002066022 see RN: 94231-42-2, 100378-58-3, 131826-14-7, 16527-70-1, 188484-10-8; 55050-49-2, 63366-02-9, 68773-55-7, 97857-01-7, 103701-47-9. ---	16
X	WO 95 31512 A (ZENECA LIMITED) 23 November 1995 see examples 1-2 & DATABASE CHEM. ABS. REGISTRY American Chemical Society see RN: 76392-25-1 ---	16
X	WO 95 00560 A (K.L. JOHNSON; UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY CORP.) 5 January 1995 see page 9; example 19 X see page 14 - page 15 & DATABASE CHEM. ABS. REGISTRY American Chemical Society see RN: 125566-99-6 see abstract ---	16 22,24
X	CHEMICAL ABSTRACTS, vol. 116, no. 10, 9 March 1992 Columbus, Ohio, US; abstract no. 84740, XP002066020 see RN (Database Registry): 86311-28-6 Y see abstract & S. TESHIGAHARA ET AL.: TOSO KENKYU HOKOKU, vol. 35, no. 2, 1991, pages 47-56, ---	16 1
	-/--	

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/07286

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 9251 Derwent Publications Ltd., London, GB; AN 92-420422 XP002066024 & JP 04 316 566 A (TOSOH CORP.) , 6 November 1992	16
Y	see abstract & DATABASE CHEM. ABS. REGISTRY American Chemical Society see RN: 147768-61-4, 129197-67-7 ---	1
Y	EP 0 468 840 A (ATOCHEM) 29 January 1992 see claim 1 & US 3 459 775 A cited in the application & US 5 283 360 A cited in the application ---	1
Y	DATABASE WPI Week 9343 Derwent Publications Ltd., London, GB; AN 93-339772 XP002066025 & JP 05 247 120 A (TOSOH CORP.) , 24 September 1993 see abstract ---	1
Y	DE 36 02 254 A (BASF A.G.) 30 July 1987 see claim 1 ---	1
Y	EP 0 109 273 A (MONTEDISON S.P.A.) 23 May 1984 see claims 15-18,35 ---	1
Y	Y. FORT ET AL.: TETRAHEDRON, vol. 48, no. 24, 1992, OXFORD GB, pages 5099-5110, XP002066250 see the whole document ---	1
X	EP 0 434 546 A (ATOCHEM) 26 June 1991 see examples 11,12	16
Y	see claim 1; examples & DATABASE CHEM. ABS. REGISTRY American Chemical Society see RN: 137621-13-7, 137620-11-5 ---	1
X	DE 39 16 035 A (KANSAI PAINT CO., LTD.) 30 November 1989 see claims ---	22,24
15 X	EP 0 604 364 A (CIBA-GEIGY A.G.) 29 June 1994 see claim 8 ---	24
3	---	

-/--

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/07286

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 733 637 A (DOW CORNING TORAY SILICONE CO., LTD.) 25 September 1996 see abstract ---	24
X	EP 0 735 066 A (DOW CORNING SILICONE CO., LTD) 2 October 1996 see abstract ---	24
X	EP 0 392 029 A (TOSOH CORPORATION) 17 October 1990 see claims 9-14 -----	24,26

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 97/07286

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1,16,21,22
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Claims Nos.: 1,16,21,22

Expressions like "cyclic moiety" for Z and "divalent linking group" for R2 used in the claims are too vague to allow a comprehensive and satisfactory search which is economically reasonable (See Guidelines for Examination in the EPO, B-III, 2). Consequently the search has been limited to the scope illustrated by the examples.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/07286

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 1418698 A	10-10-1968	GB 984827 A	
US 3230202 A	18-01-1966	NONE	
EP 479166 A	08-04-1992	CA 2052381 A	29-03-1992
		CA 2052391 A	29-03-1992
		JP 5170753 A	09-07-1993
WO 9531512 A	23-11-1995	AU 2349595 A	05-12-1995
		US 5691400 A	25-11-1997
WO 9500560 A	05-01-1995	AU 7248794 A	17-01-1995
EP 468840 A	29-01-1992	FR 2664272 A	10-01-1992
		AT 151420 T	15-04-1997
		CA 2046373 A	07-01-1992
		DE 69125540 D	15-05-1997
		DE 69125540 T	13-11-1997
		DK 468840 T	20-10-1997
		EP 0720978 A	10-07-1996
		ES 2100938 T	01-07-1997
		JP 10067690 A	10-03-1998
		JP 2693287 B	24-12-1997
		JP 6116254 A	26-04-1994
		US 5510516 A	23-04-1996
		US 5283360 A	01-02-1994
DE 3602254 A	30-07-1987	EP 0232752 A	19-08-1987
		JP 62178578 A	05-08-1987
EP 109273 A	23-05-1984	CA 1216134 A	06-01-1987
		DE 3375573 A	10-03-1988
		JP 2022939 C	26-02-1996
		JP 5177143 A	20-07-1993
		JP 7047128 B	24-05-1995
		JP 1706142 C	27-10-1992
		JP 3074235 B	26-11-1991
		JP 59108793 A	23-06-1984
		US 4562276 A	31-12-1985
		US 4595671 A	17-06-1986

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/07286

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 434546 A	26-06-1991	FR 2656304 A	28-06-1991
		CA 2033047 A	23-06-1991
		DK 434546 T	14-06-1993
		ES 2055380 T	16-08-1994
		JP 5092962 A	16-04-1993
		US 5481012 A	02-01-1996
DE 3916035 A	30-11-1989	JP 1289819 A	21-11-1989
		JP 1289820 A	21-11-1989
		CA 1339485 A	30-09-1997
		GB 2219591 A,B	13-12-1989
		US 5002977 A	26-03-1991
EP 604364 A	29-06-1994	AT 163438 T	15-03-1998
		AU 683002 B	23-10-1997
		AU 1009097 A	06-03-1997
		AU 672645 B	10-10-1996
		AU 5263993 A	07-07-1994
		CA 2112010 A	24-06-1994
		DE 59308175 D	02-04-1998
		JP 6228271 A	16-08-1994
		US 5468886 A	21-11-1995
		US 5599651 A	04-02-1997
EP 733637 A	25-09-1996	JP 8259574 A	08-10-1996
		US 5614640 A	25-03-1997
EP 735066 A	02-10-1996	JP 8269293 A	15-10-1996
		US 5658965 A	19-08-1997
EP 392029 A	17-10-1990	DE 68914140 D	28-04-1994
		DE 68914140 T	12-01-1995
		WO 9003987 A	19-04-1990
		US 5204425 A	20-04-1993
		JP 3157410 A	05-07-1991